The Center for Molecular Electrocatalysis
EFRC Director: R. Morris Bullock
Lead Institution: Pacific Northwest National Laboratory

Mission Statement: We seek to understand, predict, and control the intra- and intermolecular flow of protons in electrocatalytic multi-proton, multi-electron processes of critical importance to a wide range of energy transformation reactions, including production of H_2, oxidation of H_2, reduction of O_2, and reduction of N_2, by studying how proton relays regulate the movement of protons and electrons within and between molecules to enhance rates of electrocatalysis.

Electrocatalysts that efficiently convert electrical energy into chemical bonds in fuels, or the reverse, converting chemical energy to electrical energy, will play a vital role in future energy storage and energy delivery systems. Electrocatalytic processes involving multi-proton and multi-electron redox reactions are pervasive in energy science. The Center for Molecular Electrocatalysis will address fundamental challenges in understanding how molecular electrocatalysts function, and will use this knowledge to rationally design new classes of molecular electrocatalysts for important energy storage and utilization reactions. Closely coupled experimental and theoretical studies will include inorganic synthesis, ligand design, mechanistic studies, electrochemical measurements, determination of thermochemical values for metal hydride complexes, and evaluation of catalytic activity.

Electrocatalytic reactions to be studied include the production of hydrogen, oxidation of hydrogen, reduction of oxygen, and reduction of nitrogen. These critical reactions range from two-proton, two-electron processes to six-proton, six-electron reactions. A unique approach in this Center will be a focus on proton relays, which are functional groups (typically amine bases) that play a crucial role in the delivery of protons to (or from) the active site of molecular catalysts. Catalysts containing proton relays developed by researchers at PNNL exhibit activities for hydrogen production comparable to those of the NiFe hydrogenase enzymes used in Nature, far surpassing other synthetic catalysts. *The prevalence in energy science of reactions that require controlled movement of protons and electrons presages an immense scope for the roles of proton relays.*

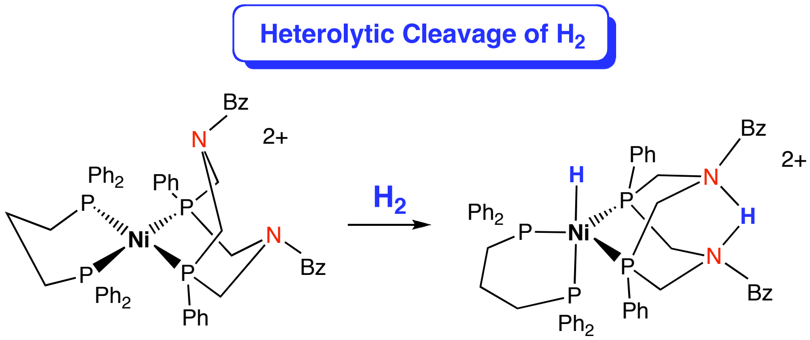
The reduction of protons derived from water to form hydrogen is the simplest fuel generation reaction (eq. 1, forward direction). The reverse process, the oxidation of H_2, is an important reaction in hydrogen fuel cells. The four-electron reduction of O_2 to form water, (eq. 2, forward direction), is important in almost all currently used fuel cells, providing the reductive half-reaction to balance the oxidative half-reaction. The opposite process, (eq. 2, reverse direction), the four-electron oxidation of water to form O_2, is required for water splitting, and has been intensively studied in connection with solar energy utilization.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad (1)$$

$$O_2 + 4\,H^+ + 4\,e^- \rightleftharpoons 2\,H_2O \qquad (2)$$

$$N_2 + 6\,H^+ + 6\,e^- \rightleftharpoons 2\,NH_3 \qquad (3)$$

Reduction of nitrogen to give ammonia (eq. 3, forward direction) is a six-electron process. This reaction is already of global importance; the Haber-Bosch process for conversion of nitrogen to ammonia consumes about 1% of the world's total energy supply, and contributes enormously to our ability to provide food for the world's growing population.



Molecular catalysts offer a degree of precise structural control – and therefore the precise probing of relationships between catalyst structure and activity – that are not possible for either heterogeneous catalysts or enzymes. *It is precisely this structure-activity knowledge that we are seeking to develop*. The two-, four-, and six-*electron* redox processes in eqs. 1-3 for H_2, O_2, and N_2, are also two-, four-, and six-*proton* processes. Facile and controlled movement of both electrons *and* protons from solution to substrates bound at the active metal site is essential for these electrocatalytic reactions. Proton transfers will need to be very carefully controlled and designed. The generality of proton transfer processes in almost all fuel generation and utilization reactions makes understanding these processes at a fundamental level of enormous importance.

Proton relays are functional groups that play a crucial role in the delivery of protons to (or from) the active site of catalysts. They are thought to play an important role in hydrogenase enzymes, the oxygen-evolving complex, and other biological systems.

Our goals at the Center for Molecular Electrocatalysis are to:

- Obtain a fundamental understanding of how proton relays accelerate proton transfers, both intra- and intermolecularly
- Understand how proton transfers can be coupled with electron transfers to accelerate catalytic reactions
- Demonstrate that a comprehensive understanding of proton relays can be used to design highly active molecular electrocatalysts for vital reactions required for a secure energy future.

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